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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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R C van Dijk



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Two component curable compositions

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## TWO COMPONENT CURABLE COMPOSITIONS

### Technical Field :

5 The present invention relates to curable compositions containing at least two components; each component contains materials (generally monomers/oligomers/polymers) that react with materials in the other component to form a cured resin. For simplicity, such compositions will be referred to as "two component" systems, since there will generally be only two components, but it will be understood that  
10 more than two components can be used and the "two component" should be understood accordingly.

When the two components are mixed, they form a resin that cures; the curing time will depend on many factors e.g. the nature of the curable materials and the ambient  
15 temperature. Examples of 2-component resins include epoxy/amine; epoxy/acrylic/amine and isocyanate/polyol systems and also hybrid systems such as epoxy/isocyanate-polyol/amines; epoxy/anhydride; and cyclocarbonate/epoxy/amine systems. Such materials are used in a wide variety of fields, for example adhesives, modelling pastes, coatings, sealants, putties, mastics, stopping compounds, caulking materials,  
20 encapsulants and surface coatings such as paints.

### Background Art

Two-part components are widely used in many industries for many purposes, including:

25 1) Model making: Within the automotive, aerospace and marine industries there is a need to produce dimensionally accurate master models, particularly of large format. These models are used by engineers for the conceptual design of the individual components utilised in the final product. More and more, such models are tested for technical and functional use, thus requiring technical material properties.

30 US-5,707,477 and US-5,773,047 describe a method for making prepreg parts for use in the aerospace industry where pliable solid patties prepared from syntactic epoxy material

are hand-applied to a block made by stacking successive layers of aluminium honeycomb core. The entire resulting structure is then heated to effect cure of the patties. However, this approach is again labour intensive, in that it involves hand application of the pliable solid patties to the honeycomb core. It also requires heating of the entire structure in order to cure the applied patties. The resulting models are also of relatively high density.

WO02/20261 describes a method of making models by making a sub-structure, applying a foamed mixed two-component resin (epoxy/amine or isocyanate/polyol systems) to the substructure to form a continuous layer, curing the resin and machining or hand cutting the cured resin to shape. This method is referred to as "net size casting" using a "seamless modelling paste" (SMP). The paste includes a thixotropic agent to increase the thixotropy of the paste after mixing and dispensing onto the substructure to ensure that the paste does not sag during curing. Amines are given as examples of suitable thixotropic agents.

15

2) Adhesives In the aerospace, auto, rail, structural and other industries, two-part adhesives are widely used, e.g. in wind turbine blade bonding and to bond other structures. Thixotropic and gap filling adhesives are of special interest for successful bonding of large structures in order to achieve even, stress-free bonding, without flow out at the edges of the structures being bonded. Thixotropic high strength adhesives are also useful if they can be dispensed as 'ropes' onto vertical or slanting surfaces to adhere protective barrier panelling, e.g. on the sides of liquid gas tanks or fuel carriers

3) Component manufacture Two-part curable resins are also used to form heavy electrical mouldings. Of especial interest are flowable thermosetting compositions which can mix very well, set and cure evenly in the casings of large transformers.

4) Paints and coatings Two-part curable resins are also used to form paints, e.g. automotive paints, and coatings and mouldings.

30

The above are given as examples of the use of two-component curable resins but the list is by no means exhaustive.

It is important that the individual components are flowable so that they can readily be mixed, especially when using machines that both mix and dispense the mixed composition. This sets certain limits on the viscosities that can be utilised and, in turn,  
5 sets limits on fillers and thixotropic agents that can be used, ultimately setting limits on the final properties that can be reached.

In many applications there is a need for the two-component composition to have a high viscosity shortly after mixing to provide a resistance to slump, i.e. a change in shape once  
10 the mixed composition has been placed in a desired location. The degree of non-slumping required can even be that of retaining almost exactly the shape and dimensions achieved by extruding the compositions through a shaped orifice. This non-slump texture is frequently obtained by dispersing a thixotropic agent such as a hydrophilic fumed silica in one of the components to blends, provided sufficient thixotropic agent is used,  
15 that generally retain their shape and non-slump properties until they are gelled and cured.

However, adding agents to increase the viscosity after mixing generally requires the individual components to also have high viscosities, even though they are thixotropic to a degree and hence have lower viscosities under shear than under no shear. The high  
20 viscosities of the components leads to difficulty in mixing the components together especially when mixing is achieved automatically during the dispensing of the mixture, leading to poor mixing of the components and hence a reduction in the properties of the cured resin. This is especially true when using platelet nanofillers that increase the viscosity of compositions substantially, even at low loadings if highly dispersed. The  
25 general problem underlying the present invention is to provide a two component composition containing platelet nanofillers that can more readily be mixed, even at high nanofiller loadings. Another aspect of the problem underlying the present invention is to provide a two component composition that, when mixed, has good anti-slumping properties and therefore has a high viscosity at rest while at the same time the individual  
30 components have a relatively low viscosity to ensure good mixing.

It has now been found that two-component compositions with platelet nanofillers present

in both components (or in at least two components for a multi-component composition) are easier to mix. In addition, it has been found that the mixed composition can have unexpectedly higher viscosities than the individual components have. This opens the way to making curable two part compositions having, when the components are mixed, high viscosities (and hence good anti-slump properties) from components that have relatively low viscosities, allowing them to be readily mixed. This invention therefore unexpectedly extends considerably the capability to use modern thixotropes synergistically within the application process, such that both the requirements for mixing and applying the mixed components and for the final cured product can be expanded.

10

In 1990, researchers at TOYOTA Central Research & Development Laboratories (Japan) [a] Fukushima, Y. et al., *J. Inclusion Phenom.*, 1987, 5, 473, b] Fukushima, Y, et al., *Clay Miner.*, 1988, 23, 27, c] Usuki, A. et al., *J. Mater. Res.*, 1993, 8, 1174, d] Yano K. et al., *J. Polym. Sci. Part A: Polymer Chem.*, 1993, 31, 2493, e) Kojima, Y. et al., *J. Polym. Sci. Part A: Polymer Chem.*, 1993, 31, 983] disclosed the enhancement in mechanical properties of nylon when clay nanocomposites are mixed into it.

Researchers have concentrated on four nanoclays as potential nanoscale particles: a) hydrotalcite, b) octasilicate, c) mica fluoride and d) montmorillonite. The first two have limitations both from a physical and a cost standpoint. The last two are used in commercial nanocomposites. Mica fluoride is a synthetic silicate, montmorillonite (MMT) is a natural one. The theoretical formula for montmorillonite is:

20



Ionic phyllosilicates have a sheet structure: At the Angström scale, they form platelets, which are 0.7-1 nm thick and several hundred nanometers (about 100-1000 nm) long and wide. As a result, individual sheets have aspect ratios (Length/Thickness, L/T) varying from 200-1000 or even higher and, after purification, the majority of the platelets have aspect ratios in the 200-400 range. In other words, these sheets usually measure approximately 200x1 nm (LxT). These platelets are stacked into primary particles and these primary particles are stacked together to form aggregates (usually about 10-30µm in size). The silicate layers form stacks with a gap in between them called the "interlayer"

30

or "gallery". Isomorphic substitution within the layers ( $Mg^{2+}$  replaces  $Al^{3+}$ ) generates negative charges that are counterbalanced by alkali or alkaline earth cations situated in the interlayer. Such clays are not necessarily compatible with polymers since, due to their small size, surface interactions such as hydrogen bonding become magnified. Thus, the ability to disperse the clays within some resins is limited and at the beginning, only hydrophilic polymers (e.g. PVA) were compatible with the clays because silicate clays are naturally hydrophilic. But, it was found that the inorganic cations situated in the interlayer can be substituted by other cations. Cationic exchange with large cationic surfactants such as alkyl ammonium-ions, increases the spacing between the layers and reduces the surface energy of the filler. Therefore, these modified clays (organoclays) are more compatible with polymers and form polymer-layered silicate nanocomposites. Various companies (e.g. Southern Clays (of 1212 Church Street, Gonzales, Texas USA 8629), Süd Chemie, Nanocor, etc.) provide a whole series of both modified and natural nano clays, which are montmorillonites. Apart from montmorillonites, hectorites and saponites are the most commonly used layered silicates.

A nanocomposite is a dispersion, often a near-molecular blend, of resin molecules and nanoscale particles. Nanocomposites can be formed in one of the following three ways: a) melt blending synthesis, b) solvent based synthesis and c) *in-situ* polymerization, as is known in the art.

There are three structurally different types of nanocomposites: 1) intercalated (individual monomers and polymers are sandwiched between silicate layers) 2) exfoliated (a "sea" of polymer with "rafts" of silicate), and 3) end-tethered (a whole silicate or a single layer of a silicate is attached to the end of a polymer chain).

There has been immense activity in the use of nano clay composites in recent years, for use in polyolefins, methacrylates (e.g. PMMA), polyamides, bio-polymers, polyurethanes, phenols, polycarbonates, to achieve benefits and claims have been made for increase in strength, flame retardency, and barrier protection and high temperature resistance.

US Patent No 6,579,927 details the formation of a nanomaterial where the clay material is homogeneously distributed throughout the polymeric matrix. The resultant nanocomposites could be moulded via injection moulding or extrusion processes.

5 The incorporation of nano clay materials into polymer matrices, to enjoy the above benefits, is not straight forward, however. The highly anisotropic nature and large surface area of nano clays can give problems in processing of polymers, particularly where 2 component reactive systems are envisaged. High loadings of the nano clay can result in unacceptably high viscosities, yet high viscosity is what is sought to achieve anti-slump characteristics in reactive systems.

10 The problem underlying the present invention is to develop two component systems where the components individually are of reasonably low viscosity for ease of processing, particularly for machine dispensed materials, yet which develop high viscosity when the components are mixed together to form a resin that is undergoing curing.

15 We have found that such a property can be achieved from particular blends of platelet additives, e.g. nano clays, and other fillers for two component reactive systems, combined with distribution of the nano clay material between the two components. Unexpectedly, exceptional non-slump characteristics are achieved indicating a synergism between the blended platelet additives and the curable resin matrix, over and beyond  
20 simple addition effects.

WO 02/42391 details the formation of a soybean oil based composites and the formation of solid three dimensional structures by solid freedom fabrication extrusion. A montmorillonite clay was blended into a resin component which contained epoxidized soy bean oil and fibrous fillers. This resin component was subsequently mixed with a  
25 curing agent such as triethylenetetramine, polyoxypropylenetriamine (Jeffamine D 230), to form a resultant paste for extrusion.

US 6,197,849 details the formation of organophilic phyllosilicates by the treatment of naturally occurring or synthetic phyllosilicates with a salt of a quaternary or other cyclic



amindine based compound. The patent covers the use of these organophilic phyllosilicate in the formation of nanocomposites, shapable moulding compounds, coatings, adhesives, casting resins, flame retardants, agents with thixotropic effect. However, the organophilic phyllosilicates are used in either the resin or hardener but there is no  
5 mention of including the organophilic phyllosilicates in each of the component at the same time

#### SUMMARY OF INVENTION:

10 One aspect of this invention relates to a composition comprising at least two reactive components that when mixed together form a reactive resin that undergoes curing, wherein the components, or at least two of the components if there are three or more components, include a filler having a platelet structure, the platelets having a thickness  
15 microns or less, preferably less than  $1\mu\text{m}$ , more preferably less than  $25\text{\AA}$  ( $\sim 2.5\text{ nm}$ ), especially less than  $10\text{\AA}$  ( $\sim 1\text{ nm}$ ), and most preferably between  $4\text{--}8\text{\AA}$  ( $\sim 0.5\text{--}0.8\text{ nm}$ ), and an aspect ratio (length/thickness) higher than 10, more preferably higher than 50 and most preferably higher than 100 or a mixture thereof. The platelets are preferably  
separable from each other under shear within the composition.

20 The present invention also provides a method of mixing the reactive components of the composition defined in the preceding paragraph.

The nanoscale platelet filler may be in the form of a nanocomposite, which is a  
25 dispersion of such a filler in a polymer or resin. The filler may be mica or glass flakes or a clay, e.g. a natural or modified montmorillonite.

The nanoscale platelet filler should, as specified above, be present in at least two of the reactive components. Preferably no one component should contain more than 80% by  
30 weight of the platelet filler content of the final cured resin since that would generally increase the viscosity of that component to an unacceptably high level. More preferably, the maximum loading of the platelet filler in any one component is 75%, e.g. 60% by weight or less of the total platelet filler content of the final cured resin. Each component

preferably includes 0.5 to 10% by weight of the platelet filler, more preferably 1 to 7%, e.g. 2 to 4%.

The nanoscale platelet filler may be surface treated, e.g. with amines, surfactants, reactive materials, (e.g. silanes or siloxanes) to make them compatible with the other ingredients of the component it is incorporated in. Especially preferred are platelet fillers treated with alkyl quaternary ammonium ions that are retained on their surface. Such fillers are commercially available, e.g. Garamite 1958 obtainable from Southern Clay Products Inc.

It has been found that the viscosity of curable compositions formed by mixing two reactive components together can be substantially increased as compared to the viscosities of the individual components if, in addition to the platelet filler, minerals, e.g. calcium carbonate, aluminium trihydrate, talc and silicas, which interact with the platelet fillers are incorporated into one or more, and preferably each, of the components. Especially preferred are (a) platelet fillers that have been subject to ion exchange, e.g. to incorporate ammonium ions such as alkyl quaternary ammonium ions, and (b) minerals such as talc, calcium carbonate and silicas that interact with the ammonium-containing platelet filler.

Typical densities of the cured resin containing mineral filler alone will be ~1 to 3 g/cc.

Additional thixotropes may also be added in the form of a silica gel, which preferably contains various siloxane and silanol groups.

It is not required to use the same nanoscale platelet filler in the various components and different platelet materials could be used. In addition, mixes of platelet materials could be incorporated into any of the components.

The two reactive components may be chosen from the components of any thermosetting resin and preferably belong to one of the following reactive systems:

- Epoxy/Amine

- Epoxy/Acrylic/Amine
- Isocyanate/Polyol

Alternative hybrid systems may be used, e.g.:

- 5 • epoxy/isocyanate- polyol/amines
- Epoxy/Anhydride
- Cyclocarbonate/epoxy/amine

10 The components may be foamable to reduce the weight of the cured resin by incorporating a foaming agent in one or more of the components and/or by frothing the mixed resin by mechanical stirring and/or blowing gas, e.g. air, into it. The foaming agent is preferably thermal- or radiation-activated to produce gas bubbles to expand the matrix of the resin.

15 The molecular weight and functionality of the monomer/oligomer/polymer content of the components should be chosen to give appropriate properties, e.g. densities, in the final cured resin. A range of different molecular weights may be used.

20 Other fillers may be incorporated into the components such as microballoons, which are glass or polymeric hollow spheres, and can be used to achieve a cured resin having a lower density, e.g.  $\sim 0.4$  to  $0.9\text{g/cc}$ . Air or gas can be introduced into the resin being cured either by foaming agents or by mechanically frothing.

25 The components may be mixed manually or mechanically, e.g. using a planetary mixer, but it is preferred to mix the components by static mixing, i.e. dispensing the components from separate component cartridges into a common conduit, where the components are mixed as they pass through the conduit; static blades in the conduits may assist in the mixing process.

30 The viscosities of the separate components (measured at a frequency of  $0.01593\text{ Hz}$  under the conditions discussed later in connection with the specific Examples) are

preferably less than 300,000 Pa.s; the viscosity of the resin immediately after thorough mixing of the components preferably exceeds 500,000 Pa.s .

5 The resin formed by mixing of the components may be cured at room temperature, which will generally be the case for large structures e.g. aerodynamic wings, wind turbine blades etc, or at elevated temperatures to accelerate the curing, depending on the resin components.

10 The cured resin may be formed to a desired shape, e.g. to form a model, by machine, e.g. using a CAD-controlled machine tool or by hand and the resin may also be trimmed.

The cured resin may be in any desired form or shape, e.g. a coating or paint covering, an adhesive deposit (as a film, powder , rope or a three dimensional structure or coherent insert), a paste or putty, or a board that can be subsequently machined.

15 Even when slump is not an especial problem in a given application, e.g. in the formation of an adhesive deposit joining two parts, the high viscosity of the resin as it is curing may well be advantageous, e.g. to keep it in place, especially when applied to vertical or slanted surfaces or the underside of a substrate.

20 The platelet filler may be a modified or unmodified nanoclay or a nanocomposite; such fillers have already been described above.

A nanocomposite is a dispersion, often a near-molecular blend, of polymer or curable resin molecules and nanoscale particles. Nanocomposites can be formed, as is known in 25 the art, in one of the following three ways: a) melt blending synthesis, b) solvent based synthesis and c) *in-situ* polymerization, as is known in the art.

There are three structurally different types of nanocomposites: 1) intercalated (individual monomers and polymers are sandwiched between silicate layers) 2) exfoliated (a "sea" of polymer with "rafts" of silicate), and 3) end-tethered (a whole silicate or a single layer of 30 a silicate is attached to the end of a polymer chain).

It is important that the platelet filler should be compatible with the compositions of the resin components so that the filler will disperse as individual platelets or a thin stack of platelets in the components. The compatibility can be achieved by a suitable choice of the filler and in particular, in the case of clay compositions, the nature of the surface groups on the particles of clay materials; surface groups can be incorporated by means of an ion exchange process, which can result in the addition of, for example, ammonium quaternary ions to the surface of the platelet clays. A particular clay of interest that can be used with a broad range of two component compositions is Garamite 1958. Garamite 1958 is a modified nanoclay and has alkyl quaternary ammonium ions on the surface of a basic bentonite clay structure.

The organically modified silicate Garamite 1958 is commercially available and is used as a rheological additive in numerous polymer systems such as epoxies and unsaturated polyesters. The addition of Garamite 1958 has been observed to increase the thixotropy of polymer systems and reduce the tendency for sag. This rheological additive can be used as an alternative to other thixotropic agents such as fumed silica.

As shown in the subsequent examples, the presence of platelet fillers, e.g. Garamite 1958, within the reactive components of a two part resin composition results in the formation of relatively low viscosity pastes possessing a cream like consistency. It has been found surprisingly that when the two components of the two part resin composition both contain this rheological agent and are mixed together in varying proportion (such as 1:1 and 2:1) to form a resin undergoing curing, the resin has an unexpected and significant relatively high viscosity. This phenomenon imparts an advantageous degree of slump resistance.

In one embodiment, one of the reactive components preferable comprises an epoxy resin and the other component includes a hardener for the epoxy resin, e.g. a polyamine or a polyol, or poly-anhydride, or polycyclocarbonate, or hybrids thereof.

The epoxy resin may consist of one or more epoxy resins that are themselves liquid or may be a liquid mixture of one or more solid epoxy resins with one or more liquid epoxy

resins or may be one or more solid epoxy resins dissolved in a diluent; diluents are conventionally used in epoxy resin compositions and are well-known. The epoxy resin may be a polyglycidyl ether of a polyhydric alcohol such as 1,4-butanediol or 1,3-propanediol or, preferably, a polyglycidyl ether of a polyhydric phenol, for example a bisphenol such as bis(4-hydroxyphenyl)methane (bisphenol F) or 2,2-bis-(4-hydroxyphenyl)propane (bisphenol A) or a novolak formed from formaldehyde and a phenol such as phenol itself or a cresol, or a mixture of two or more such polyglycidyl ethers. Polyglycidyl ethers of bisphenol A are especially preferred. The epoxy resin, particularly where it comprises a solid epoxy resin, may contain one or more epoxy-functional diluents, usually monoepoxides, or non-epoxide diluents, such as the monoepoxide and non-epoxide diluents conventionally used in curable epoxy resin compositions.

Examples of amines suitable for use as the amine hardener include those aliphatic, cycloaliphatic, aromatic, araliphatic and heterocyclic amines known as hardeners for epoxy resins, including: alkylenediamines such as ethylenediamine or butane-1,4-diamine; polyalkylenepolyamines such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, dipropylenetriamine or tripropylenetetramine; N-hydroxyalkyl derivatives of polyalkylene polyamines such as N-(hydroxyethyl) diethylenetriamine or mon-N-2-hydroxypropyl derivative of triethylenetetramine; polyoxyalkylenepolyamines such as polyoxyethylene – and polyoxypropylene – diamines and triamines; N,N-dialkylalkylenediamines such as N,N-dimethylpropane-1,3-diamine or N,N-diethylpropane-1,3-diamine; cycloaliphatic amines having an amino or aminoalkyl group attached to the ring, such as 3-aminomethyl-3,5,5-trimethylcyclohexylamine (isophoronediamine); aromatic amines such as bis(4-aminophenyl)methane or bis(4-aminophenyl)sulphone; amine-terminated adducts of epoxy resins with aliphatic, cycloaliphatic or araliphatic amines as hereinbefore described; N-aminoalkyl-piperazines such as N-(2-aminoethyl)piperazine or N-(3-aminopropyl)piperazine; and polyaminoamides, for example reaction products of polyalkylenepolyamines such as those hereinbefore mentioned with polymerised unsaturated fatty acids, e.g.. polymerised vegetable oil acids such as dimerised or trimerised linoleic or ricinoleic acids; or a mixture of two or more of such amines.

Aliphatic and cycloaliphatic amine hardeners are usually preferred, including N-hydroxyalkyl derivatives of polyalkylene polyamines, particularly a mono-N-2-hydroxypropyl derivative of triethylenetetramine, and mixtures thereof with

5 polyaminoamide reaction products of polyalkylenepolyamines and polymerised vegetable oil acids and the amine functional reaction products of amines and epoxy group containing compounds. The amount of amine hardener is preferably such as to provide from about 0.75 to 1.25 amino hydrogen equivalents per 1,2-epoxide equivalent of the epoxy resin (1).

10

The hardener may have a dendrimeric structure (e.g. with functional amine, hydroxy or acidic reactive groups).

The components may also contain minor amounts of accelerators (e.g. tertiary amines,

15 etc) and latent hardeners (e.g. dicyanamide, or boron – amine complexes) and additives conventionally used in the particular application, such as diluents, fillers (such as calcium carbonate), fibers, pigments, dyes, fire retardants, antifoaming agents, wetting agents and polymeric toughening agents. Preferably, the paste additionally includes molecular

20 sieves, which function as moisture scavengers, and are well known to those skilled in the art, examples being zeolites with open-network structures. Preferably, the paste also includes surfactants or antifoaming agents such as a silicone surfactant like Dabco DC 197 Surfactant, available from Air Products, though other products are commercially available and well known to those skilled in the art. It has also been found that the

25 addition of calcium stearate improves the machinability of the cured material and so its addition is also advantageous. These auxiliary materials may be conveniently added with any or all of the components.

Techniques for mechanically mixing the components of a curable two-part curable resin, e.g. modelling pastes, and dispensing the mixed resin are known in the art, e.g. by using

30 Tartler Nodopox machinery. The bulk density of the resulting cured articles is usually 0.8 to 1.3 g/cm<sup>3</sup>, although this will depend on the weight of any filler used, as discussed above.

Conveniently, separate tanks are filled with the two components, e.g. resin and hardener. The application of low pressure to the tanks facilitates pumping of the materials. Preferably, pumps deliver the components from the tanks to a mixing block where they  
5 are mixed. The residence time in the mixing block, the speed of mechanical stirring and the length of the hose attached to the chamber influence the homogeneity of the mixture.

The present invention can be used to make a seamless model free of bond lines; typical steps in making such models are:

- 10 1. providing a substructure having an exposed outer surface,
2. applying a modelling paste to the outer surface of the substructure in the form of a continuous layer,
3. curing the continuous layer of applied modelling paste, and
4. machining said cured layer of modelling paste to the desired contour.

15

Cure of the curable resin can be effected in accordance with conventional practice in the particular application. In general, the composition can be allowed to gel (set) at ambient temperature or heated moderately in accordance with conventional practice to accelerate setting. Subsequently, completion of cure may be effected at ambient temperature,  
20 moderately elevated temperature or higher temperature as required. Typically, room temperature cure is preferred.

#### EXAMPLES:

25

The materials of Table 1 are referred to in the following description:



Table 1. Raw Materials

Raw Material	Description of Material	Supplier
Araldite GY 260	Bisphenol A epoxy resin	Huntsman Group Vantico Limited
Araldite GY 281	Bisphenol F epoxy resin	Huntsman Group Vantico Limited
IP 262	Isophorone diamine/ Trimethylhexamethylenedia mine adduct	Huntsman Group Vantico Limited
IP 271	Isophorone diamine/ Jeffamine D 230 adduct	Huntsman Group Vantico Limited
Diocetyl adipate	Di (2-ethylhexyl)adipate	Petrochem UK Ltd
Araldite DY H/BD	Diglycidylether of 1.6 hexenediol	Huntsman Group Vantico Limited
Apyral 22/33	Aluminium hydroxide	Nabaltec
Sphericel 110 P8	Borosilicate glass	Potters industries
Q Cel 5028	Silicic acid, sodium salt, boric acid sodium salt, siloxane	Potters industries
Creta fine N 100	Calcium carbonate	Needham Minerals Limited
Coathylene TB 2957	Ethylene-acrylate-acrylic acid copolymer	Dupont Polymer Powders SA
Calofort S	Stearate coated calcium carbonate	Omya UK
Jeffamine D 230	Polyoxypropylenediamine	Huntsman
Ruetasolv DI	Diisopropyl naphthalene isomers	Rutgers Kureha Solvents. GmbH
Accelerator 399	Triethanolamine, piperazine, aminoethylpiper azine	Huntsman
Aerosil R202	Silicones and siloxanes, dimethyl-reaction products with silica	Degussa AG
Aerosil R 8200	Silanamine,hydrolysis products with silica	Degussa AG
Bentone SD-2	Organic derivative of a montmorillinite clay	Elementis Specialties
PJ 755	Titanium dioxide/ black iron oxide	PJ Colours Ltd
Garamite 1958	Alkyl quaternary ammonium clay	Southern Clay Products Inc
Tetraethylene pentamine (TEPA)	Tetraethylene pentamine	Dow Chemical Company Ltd
Aradur 140	Polyamidoimidazoline	Huntsman Group Vantico Limited

None of the fillers used in the formulations stated in Tables 2-4 and 7-8 have undergone any specific drying procedure before being utilized in the manufacture of these specific constituents.

## 5 Experimental Procedure

In this specification, all percentage values are percentages by weight.

### Formulations 1 to 3

10 A general process was used for the manufacture of a first formulation (Formulation 1) of a two-part composition, comprising an epoxy resin component and a hardener component. The epoxy resin component is formed in a disperser type mixer as follows:

1. Charge GY 260 (39.520%), GY 281(11.530 %), Aradlite DY HB/D (1.980%), Diocetyl adipate (3.460%), Calofort S (5.930%), Apyral 22 (6.120%) and  
15 Spherichel 110 P8 (19.3%) into the disperser type mixer together with usual additives such as surfactants, antifoam agents and pigments(1.28%). Start the mixer at a sufficient speed in order to wet out the powders sufficiently.
2. Aerosil R 8200 (1.986%) and Coathylene TB 2957 (5.930%) are then added and  
20 mixture mixed for a sufficient period of time to achieve an even dispersion. A vacuum is then applied and the formulation dispersed at high speed in order to achieve a homogeneous suspension. Garamite 1958 (2.960%) is then added , a vacuum applied and the mixture dispersed at high speed at a temperature in excess of 50°C for a period of 20 minutes in order to achieve a homogeneous  
25 mixture

The same general process was adopted for the manufacture of the reactive resin components in Formulations 2, 4 and 5 described below.

The general process for the manufacture of hardener component of Formulation 1 in a  
30 disperser type mixer was as follows:

1. IP 262 (42.0%), Ruetasolv DI (3.0%), Apyral 22 (21.8%), Spherichel 110 P8 (23.0%) into the disperser type mixer together with usual additives such as

surfactants and antifoam agents (1.9%). Start the mixer at a sufficient speed in order to wet out the powders sufficiently. A vacuum is then applied and the formulation dispersed at high speed in order to achieve a homogeneous suspension

- 5    2. Coathylene TB 2957 (5.8%) and Garamite 1958 (2.5%) were then added , a vacuum applied and the mixture dispersed at high speed at a temperature in excess of 50°C for a period of 20 minutes in order to achieve a homogeneous mixture

- 10   This general procedure was also adopted in the manufacture of the reactive hardener component in Formulations 2, 4 and 5.

The general procedure for the manufacture of the reactive resin component in Formulation 3 in a planetary type mixer was as follows:

- 15   1. Charge Araldite GY260 (46.0%), Araldite GY 281 (6.0%), Araldite DY H/BD (3.76%), Dioctyl adipate (2.0%), Apyral 22 (11.48%) Cretafine N100 (10.8%), Q Cel 5028 (14.9%) and other minor ingredients such as surfactants, antifoam agents and pigments (2.3%) into a planetary type mixer. Start the mixer at a sufficient speed in order to wet out the powders sufficiently. Apply a vacuum and mix at a sufficient speed to in order to obtain a homogeneous mixture.
- 20   2. Charge Garamite 1958 (2.76%) and start the mixer at a sufficient mix in order to disperse this material evenly within the mixture. Apply a vacuum and mix this formulation at sufficient speed at a temperature above 30°C for a period time in excess of 15 minutes.

25

The general procedure for the manufacture of the reactive hardener component in Formulation 3 in a planetary type mixer was as follows:

- 30   1. Jeffamine D 230 ( 38%), Accelerator 399 (0.5%), Ruetasolv DI (4.0%), Cretafine N100 (22.50%), Apyral 22 (14.0%), Q Cel 5028 (14.7%) and other minor ingredients (0.3%) into a planetary type mixer. Start the mixer at a sufficient

speed in order to wet out the powders sufficiently. Apply a vacuum and mix at a sufficient speed to in order to obtain a homogeneous mixture.

2. Charge Aerosil R 8200 (2.0%) Garamite 1958 (4.0%) and start the mixer at a sufficient mix in order to disperse this material evenly within the mixture. Apply a vacuum and mix this formulation at sufficient speed at a temperature above 40°C for a period time in excess of 15 minutes.

Table 2 shows the compositions of the two components of Formulations 1 to 3:

Table 2: Formulation 1

<u>Resin Composition</u>	<u>Quantity (%) wt</u>	<u>Hardener Composition</u>	<u>Quantity (%) wt</u>
Araldite GY 260	39.520	IP 262 Adduct	42.000
Araldite GY 281	11.530	Sphericel 110 P8	23.000
Diocetyl Adipate	3.460	Apyral 22	21.800
Araldite DY H/BD	1.980	Coathylene TB 2957	5.800
Apyral 22	6.120	Ruetasolv DI	3.000
Sphericel 110 P8	19.30	Garamite 1958	2.500
Coathylene TB 2957	5.930	Additives	1.900
Calofort S	5.930		
Garamite 1958	2.960		
Aerosil R 8200	1.986		
Additives	1.284		

Table 3: Formulation 2

<u>Resin Composition</u>	<u>Quantity (%) wt</u>	<u>Hardener Composition</u>	<u>Quantity (%) wt</u>
Araldite GY 260	40.000	IP 271 Adduct	39.000
Araldite GY 281	10.000	Spherichel 110 P8	15.000
Dioctyl Adipate	3.500	Apyral 22	23.248
Araldite DY H/BD	2.000	Coathylene TB 2957	6.000
Apyral 22	10.000	Ruetasolv DI	4.000
Spherichel 110 P8	14.800	Garamite 1958	2.000
Coathylene TB 2957	6.500	Calofort S	8.600
Calofort S	6.000	Other minor ingredients	2.152
Garamite 1958	2.500		
Aerosil R 8200	2.000		
Other minor ingredients	2.700		

Table 4: Formulation 3

<u>Resin Composition</u>	<u>Quantity (%) wt</u>	<u>Hardener Composition</u>	<u>Quantity (%) wt</u>
Araldite GY 260	46.000	Jeffamine D 230	38.000
Araldite GY 281	6.000	Accelerator 399	0.500
Dioctyl Adipate	2.000	Apyral 22	14.000
Araldite DY H/BD	3.760	Cretafine N 100	22.500
Apyral 22	11.480	Q Cel 5028	14.700
Q Cel 5028	14.900	Ruetasolv DI	4.000
Cretafine N 100	10.800	Aerosil R 8200	2.000
Garamite 1958	2.760	Garamite 1958	4.000
Other minor ingredients	2.300	Other minor ingredients	0.300

5

**Evaluatoin of Formulations**

The pastes are evaluated as follows.

1. The slump resistance of the paste is measured immediately after mixing and prior to curing. The curing takes place immediately on mixing is not delayed and the thixotropic nature of the paste is immediately observed whilst being dispensed. by dispensing the paste utilising Tartler Nodopox machinery at a thickness of 10-50mm horizontally onto a vertical surface. This method allows evaluation of the degree of sag visually at different application thicknesses. The thickness of the

10

strips of paste are measured using a ruler . If the shape of the strips starts to distort and move down the vertical surface onto which they are applied then the material is effectively slumping. Table 6 gives values of slump resistance measured.

- 5 2. The density is measured at 23°C in accordance with ISO 1183.
3. The viscosities of the individual components of the reactive resin and the hardener and the mixture of the two were measured at 25°C using a TA Instruments Rheometer AR 2000. An internal test method is used to measure the viscosity at a frequency of 0.01593 Hz, geometry 2 cm diameter serrated plate (formulations 1-5). In the case of formulations 6-20 a 2cm diameter 2° cone and  
10 plate geometry was used. The shear rate was then increased in a continuous ramp from 1 Hz to 50 Hz over a period of one minute.
4. Linear shrinkage is measured by dispensing the mixed paste from the Tartler Nodopx into a mould with the dimensions of 1000x 60 x 40 mm. The degree of shrinkage is recorded after 7 days curing at room temperature.  
15
5. The Shore D hardness is measured on the cured samples in accordance with ISO 868.

Table 5 shows the viscosity values of the components and the mixed resin of  
20 Formulations 1 to 3; where more than one value was taken, the range of the measured values is shown in Table 5:

Table 5: Viscosity measurements of individual and mixed components

	<u>Formulation 1</u> <u>Viscosity @</u> <u>0.01593 Hz (Pa.S)</u>	<u>Formulation 2</u> <u>Viscosity @</u> <u>0.01593 Hz (Pa.S)</u>	<u>Formulation 3</u> <u>Viscosity @</u> <u>0.01593 Hz (Pa.S)</u>
Reactive resin component	135,000	56,500-106,100	3,074-7,890
Reactive hardener component	12,830	27,000 – 49,850	17, 490
Mixed components	301,800	338,000-342,000	235,500-265,000

As clearly seen, the viscosity of the mixed resin is substantially greater than that of either of the component parts. Table 6 sets out the physical properties of thixotropic seamless modelling pastes of Formulations 1 to 3

5 Table 6. Physical properties of thixotropic seamless modelling pastes

Physical Properties	Formulation 1	Formulation 2	Formulation 3
Density	1.2/1.17	1.24/1.25	0.88/0.87
Consistency	Thixotropic paste	Thixotropic paste	Thixotropic paste
Slump resistance	> 40 mm	40 mm	30 mm
Cracks	None	None	None
Shore D Hardness (Fully cured)	75	78	75-77
Linear shrinkage 1000mm length, 40 mm thickness	1mm	0.5mm	1mm

#### Comparative Formulations 4 and 5

- 10 Formulations 4 and 5, which are comparable to Formulations 1 to 3, were made but one did not include the platelet filler (Garamite) in the epoxy resin component and Formulation 5 did not include the platelet filler (Garamite) in either component. Tables 7 and 8 set out the compositions of these Formulations:

15 Table 7 : Formulation 4

<u>Resin Composition</u>	<u>Quantity (%) wt</u>	<u>Hardener Composition</u>	<u>Quantity (%) wt</u>
Araldite GY 260	42.000	IP 262 Adduct	42.000
Araldite GY 281	10.500	Sphericel 110 P8	23.000
Diocetyl Adipate	3.500	Apyral 22	21.800
Araldite DY H/BD	2.800	Coathylene TB 2957	5.800
Snowcal 40	9.670	Ruetasolv DI	3.000
Sphericel 110 P8	11.600	Garamite 1958	2.500
Coathylene TB 2957	5.830	Other minor ingredients	1.9%
Calofort S	5.000		
Bentone SD-2	2.500		
Aerosil R 8200	2.000		
Aerosil R 202	3.500		
Other minor ingredients	1.1		

Table 8 : Formulation 5

<u>Resin Composition</u>	<u>Quantity (%) wt</u>	<u>Hardener Composition</u>	<u>Quantity (%) wt</u>
Araldite GY 260	42.000	IP 262 Adduct	46.000
Araldite GY 281	10.500	Spherichel 110 P8	14.000
Dioctyl Adipate	3.500	Apyral 33	12.200
Araldite DY H/BD	2.800	Coathylene TB 2957	4.000
Snowcal 40	9.660	Airflo CC	9.000
Spherichel 110 P8	10.600	Aerosil R 202	4.000
Coathylene TB 2957	5.000	Aerosil R 8200	4.500
Calofort S	5.000	Ruetasolv DI	5.6
Bentone SD-2	3.000	Other minor ingredients	1.2
Aerosil R 8200	2.500		
Aerosil R 202	4.300		
Other minor ingredients	1.14		

- Table 9 shows the viscosity values of the components and the mixed resin of Formulations 4 and 5; where more than one value was taken, the range of the measured values is shown in Table 9

Table 9. Viscosity measurements of Formulations 4 and 5 stored at room temperature

	<u>Formulation 4</u> <u>Viscosity @</u> <u>0.01593 Hz (Pa.S)</u>	<u>Formulation 5</u> <u>Viscosity @</u> <u>0.01593 Hz (Pa.S)</u>
Reactive resin component	313,500-315,700	553,100-582,600
Reactive hardener component	14,980-25,220	2,951-5,974
Mixed components	38,880-197,700	113,100-205,600

- Table 9 shows a drop in viscosity on mixing. Table 9 clearly shows that the increased viscosity values shown in Table 5 are not due to partial curing of the Formulations.

Table 10 shows the physical properties of Formulations 4 and 5 following mixing:



Table 10: Physical properties

Physical Properties	Formulation 4	Formulation 5
Density	1.26/1.17	1.24/nd
Consistency	Thixotropic paste	Thixotropic paste
Slump resistance	> 30 mm	40 mm
Cracks	None	None
Shore D Hardness (Fully cured)	75	n/d
Linear shrinkage 1000mm length, 40 mm thickness	1mm	n/d

- This effect of heightened thixotropy when combining the individual reactive resin and reactive hardener component is only noted when Garamite 1958 (alkyl quaternary ammonium clay) is present in both components (see Formulation 4 where only one of these components i.e. the hardener contains Garamite). In Formulation 4, the reactive epoxy resin component contains two silica based thixotropes possessing various siloxane and silanol groups on the surface. A third rheological agent (Bentone SD-2) is also present and is classified as an organic derivative of a montmorillonite clay. When combined using the standard mixing and dispersing method the resultant paste does not exhibit a viscosity significantly higher than that of both individual components. Formulation 4 is similar in nature to Formulation 1. The slump resistance in Formulation 4 is lower than that of Formulation 1 which concurs with a lower mixed viscosity.
- In the case of Formulation 5, the reactive epoxy resin component again contains two silica based thixotropes possessing various siloxane and silanol groups on the surface along with an organic derivative of a montmorillonite clay (Bentone SD-2). The hardener constituent contains only two silica based thixotropes and hence no clay based thixotrope was present in this component. The reactive epoxy resin component used in Formulation 5 had a higher viscosity than the reactive epoxy resin component used in Formulation 4. However, when combined with the hardener component, Formulation 5 shows a reduction in the viscosity of the mixed system in relation to that of the individual reactive resin component of 60%. Formulation 5 is therefore another example where the absence of a particular type of clay material in both the reactive resin and hardener components

does not initiate an increase in viscosity of the mixed system in relation to the viscosity of the individual reactive components.

#### Formulations 6 to 14

- 5 As set out in Table 11, Formulations 6 to 14, which are adhesive compositions, each contained a component of a two-part curable resin, i.e. either a resin (Araldite GY260) or a hardener for the resin (Aradur 140 or TEPA). Component Formulations 9 to 14 also contained an alkyl quaternary ammonium clay (Garamite 1958) Formulations 6 to 14
- 10 were prepared by mixing the raw materials by hand at room temperature under ambient conditions until a homogeneous composition was obtained. Each resin composition was made in an amount of approximately 100g and each hardener composition in an amount of approximately 50g.

15 Table 11 Chemical composition

Component Formulation No	Quantity of GY 260 (%)	Quantity of Aradur 140 (%)	Quantity of TEPA (%)	Quantity of Garamite 1958 (%)
6	100			
7		100		
8			100	
9	98			2
10		98		2
11			98	2
12	96			4
13		96		4
14			96	4

The viscosity of Component Formulations 6 to 14 was measured using the procedures outlined above using a shear frequency of 4 Hz and the results are set out in Table 12.

Table 12: Viscosity of individual and mixed component formulations

Component Formulation No	Viscosity at 4 Hz (Pa.s)
6	12.13
7	21.05
8	0.18
9	16.79
10	24.19
11	0.21
12	25.93
13	37.77
14	0.55

Component Formulations 6 to 14 were mixed together by hand in the proportions set out in Table 13 to form curable compositions containing one resin Component Formulation (6,9 or 12) and one hardener Component Formulation (7,8,10,11,13 or 14). The viscosity of each curable composition was measured immediately after mixing using the procedures outlined above but with a shear frequency of 4 Hz and the results are set out in Table 13.

10

Table 13:

Formulation	Ratio of Resin Component Formulation (6,9 or 12) to Hardener Component Formulation (7,8,10,11,13 or 14)	Viscosity of mixed components at 4 Hz (Pa.s)
6 + 7	100: 65	14.15
6+ 8	100: 14	4.351
9 + 10	100: 65	21.23
9 + 11	100: 14	6.114
12 + 13	100: 65	37.29
12 + 14	100: 14	16.61

#### Component Formulations 15 to 20

15

As set out in Table 14, Component Formulations 15 to 20 each contained a component of a two-part curable resin, i.e. either a resin (Araldite GY260) or a hardener for the resin (Aradur 140 or TEPA). All Component Formulations also contained an alkyl quaternary ammonium clay (Garamite 1958) and fillers (Apyral 22, Calofort S and Spherichel 110

20 P8)

Table 14

Component Formulation No	Quantity (%)					
	15	16	17	18	19	20
Tetraethylene pentamine	67.2	65.2				
Aradur 140			67.2	65.2		
Araldite GY 260					67.2	65.2
Garamite 1958	2	4	2	4	2	4
Apyral 22	10	10	10	10	10	10
Calofort S	6	6	6	6	6	6
Spherichel 110 P8	14.8	14.8	14.8	14.8	14.8	14.8

The viscosities of the individual component formulations and mixtures of the formulations, as set out in Table 15 were measure using the procedure set out above at a shear frequency of 4 Hz.

Table 15: Viscosity of individual and mixed components

Formulation	Ratio of Resin Component Formulation (19 or 20) to Hardener Component Formulation (15 to 18)	Viscosity at 4 Hz (Pa.s)
15		2.975
16		13.94
17		53.37
18		80.66
19		42.38
20		51.05
19+15	100 : 14	16.51
19+17	100 : 14	61.76
20+16	100 : 65	41.19
20+18	100 : 65	124.7

The introduction of clay in the form of Garamite 1958 (concentration of 2 to 4%) into the reactive resin (formulation 6) and hardener components (formulation 7 and 8) increased the viscosity of these individual components (see Table 12). This would be expected due to the platelet like structure of the clay. Similarly, the viscosity of the reactive resin and hardener components containing nanoclay was higher than the viscosity of the mixed reactive resin and hardener constituents without nanoclays (see formulation 6 + 7 and 6+ 8 compared with 9+10 and 9+11 in Table 13 ).

The use of nanoclay and additional fillers that interact with the nanoclay (Apyral 22, Calofort S and Spherichel 110 P8) , increases the viscosity of the individual resin and

hardener components (Table 15, Formulation 15-20) compared to the corresponding formulations without the additional fillers, i.e. containing, as fillers, solely the clay constituent (Table 12 formulations 9-14). However, the viscosity of a mixture of the resin and hardener components that each contain both nanoclay and the additional fillers

5 showed an unexpected increase as compared to the viscosity recorded for individual resin and hardener components, see the combination of (a) formulations 17 and 19 and (b) formulations 18 and 20 (Table 15). This is principally the same effect observed for formulations 1, 2 and 3.

**CLAIMS:**

1. A composition comprising at least two reactive components that when mixed together form a reactive resin that undergoes curing, wherein at least two of the components each includes a filler having a platelet structure, the platelets having a thickness of less than 5 micron, preferably less than  $1\mu\text{m}$ , such as less than  $25\text{\AA}$  ( $\sim 2.5\text{ nm}$ ), more preferable less than  $10\text{ \AA}$  ( $\sim 1\text{ nm}$ ), and most preferably between  $4\text{-}8\text{ \AA}$  ( $\sim 0.5\text{-}0.8\text{ nm}$ ), and an aspect ratio (length/thickness) higher than 10, more preferably higher than 50 and most preferably higher than 100 or a mixture thereof, the platelets preferably being separable from each other under shear within the composition.
- 2.. The composition of claim 1, wherein the platelet filler is a modified or unmodified nanoclay, e.g. a natural or modified montmorillonite or bentonite, or a nanocomposite containing such a nanoclay or mica or glass flakes.
- 3.. The composition of claim 1, wherein the platelet filler is a nanoclay having ammonium ions, e.g. alkyl quaternary ammonium ions, on the surfaces of the platelets.
- 4.. The composition of any preceding claim, wherein the amount of the platelet filler present in any one component is less than 80% by weight of the platelet filler content of the final cured resin, more preferably less than 75%, e.g. 60% by weight or less of the total platelet filler content of the final cured resin.
- 5.. The composition of any preceding claim, wherein the amount of the platelet filler present in each component is 0.5 to 10% by weight, more preferably 1 to 7%, e.g. 2 to 4%.
- 6.. The composition of any preceding claim, wherein reactive components form a thermosetting composition, which is preferably selected from one of the following reactive systems:
  - epoxy/Amine;
  - epoxy/Acrylic/Amine;

isocyanate/Polyol;  
 epoxy/isocyanate- polyol/amines;  
 epoxy/Anhydride; and  
 cyclocarbonate/epoxy/amine

5

7. The composition of any preceding claim, wherein the viscosity of each of the separate components is less than 300,000 Pa s and the viscosity of the resin immediately after thorough mixing of the components exceeds 500,000 Pa s.

10

8. The composition of any preceding claim, which further includes a filler that interacts with the platelet filler, e.g. calcium carbonate, aluminium trihydrate, talc and/or silicas.

9. The composition of claim 1, which comprises:

15

as a curable resin component:

30 to 80%, preferably 40 to 60%, of a curable resin, e.g. an epoxy resin;  
 0.5 to 5%, preferably 2 to 4%, of a platelet filler, preferably a filler having ammonium ions, e.g. alkyl quaternary ammonium ions, on the surfaces of the platelets,

20

5 to 40%, preferably 10 to 30%, of a filler that interacts with the the platelet filler, e.g. calcium carbonate, aluminium trihydrate, talc and silicas, and  
 0 to 50%, of an inert filler, e.g. microballoons or glass beads, and usual additives and

as a hardener:

25

30 to 70%, preferably 40 to 60%, of a hardener for the curable resin, e.g. a compound containing two or more amine groups,

0.5 to 5%, preferably 2 to 4%, of a platelet filler, preferably a filler having ammonium ions, e.g. alkyl quaternary ammonium ions, on the surfaces of the platelets,

30

5 to 40%, preferably 10 to 30%, of a filler that interacts with the platelet filler, e.g. calcium carbonate, aluminium trihydrate, talc and silicas, and  
 0 to 60%, of an inert filler, e.g. microballoons or glass beads and usual additives.

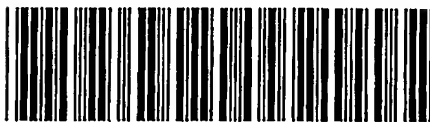
10. Use of a composition as claimed in any preceding claim as adhesives, modelling pastes, coatings, sealants, putties, mastics, stopping compounds, caulking materials, encapsulants or surface coatings, e.g. paints, or in the extrusion or jetting of three  
5 dimensional objects by layerwise deposition or in the manufacture of moulds for casting or for injection moulding or in the manufacture of modelling boards.



ABSTRACTTWO COMPONENT CURABLE COMPOSITIONS

5 A two component reactive composition is described. Each component, before they are mixed together, contains a filler having thin platelet structure; e.g. a nanoclay, and a further filler that interacts with the platelets. The individual components can have a filler loading that makes them flowable and therefore the components can readily be mixed together for ready dispensing. When the components are mixed thoroughly together, the  
10 resulting resin has a viscosity higher than that of the individual components. The loading of the filler is preferably chosen so that the resulting blended resin is capable of being applied on to a vertical surface without experiencing significant slump. The viscosity of the mixed material can be up to 5 to 10 times or more than that of the individual components before mixing. The composition can be used in adhesives, modelling pastes,  
15 coatings, sealants, putties, mastics, stopping compounds, caulking materials, encapsulants and surface coatings, e.g. paints.

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